



The mechanism behind the DOM effects on methylmercury photodegradation

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Methyl mercury (CH_3Hg^+), a neurotoxin, is the most toxic form of mercury that occurs in natural waters [1–4]. It is a cause of concern because of increasing worldwide pollution by mercury in both water and atmosphere [3, 5]. Photodegradation of CH_3Hg^+ is one of the main removal pathways from surface waters, and it has been shown to occur in the presence of dissolved organic matter (DOM) but not in ultra-pure water [2, 4]. Several mechanisms for the photodegradation of CH_3Hg^+ have been proposed, including: (1) direct photodegradation of CH_3Hg –DOM complexes via intramolecular electron transfer [4] and (2) indirect photodegradation of CH_3Hg –DOM by free radicals/reactive oxygen species such as singlet oxygen ($^1\text{O}_2$) and the hydroxyl radical (HO^\bullet) [1, 2, 6]. Studies show that the photo-Fenton reaction or the reactive oxygen species, including hydroxyl radical (HO^\bullet), $^1\text{O}_2$, triplet excited state of DOM ($^3\text{DOM}^*$), and hydrated electron (e_{aq}^-), play a minor role in CH_3Hg^+ photodegradation in aqueous media [3, 4, 6]. Interestingly, the photodegradation of CH_3Hg^+ depends on the wavelength-specific incident photon flux,

on DOM contents and salinity, but does not depend on nitrate photolysis [3]. It has been shown that rates of CH_3Hg^+ photodegradation are decreased with increasing salinity and DOM contents [3]. Increasing DOM contents with the CH_3Hg^+ aqueous media can act as a barrier to reach the incident light intensity toward the CH_3Hg^+ component which could presumably decline the rates of CH_3Hg^+ photodegradation. Several gaps still exist concerning the proposed photodegradation pathways, including two unresolved key questions: (1) how does DOM form bonds with CH_3Hg^+ ? and (2) How is the newly formed complex excited upon irradiation? A couple of considerations may help in shedding some light over this issue and could provide scope for further research in the field.

The first issue is the formation of π -electron bonding systems between CH_3Hg^+ [$\text{Hg}^{1+} = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1 4f^{14} 5d^{10}$] and DOM (CH_3Hg –DOM), through electron donation from the functional groups of high molecular weight DOM to an empty s -orbital of CH_3Hg^+ (ligand-to-metal charge transfer) [7]. Note that the π -electron bonding system is not formed with low-molecular-weight DOM, because the formed complex would not be stable enough. The overall conditional complexation constants (K'_{DOM}) between $\text{Hg}(\text{II})$ and DOM (extracted humic acids, fulvic acids and hydrophobic acids) show very strong interactions ($K'_{\text{DOM}} = 10^{23.2 \pm 1.0}$ L/kg) at Hg/DOM ratios below approximately 1 $\mu\text{g Hg}/\text{mg DOM}$, which are indicative of mercury–thiol bonds [8]. Photodegradation of methylmercury can thus occur via a pathway that involves thiol complexation [2, 4]. In contrast, much weaker interactions ($K'_{\text{DOM}} = 10^{10.7 \pm 1.0}$ L/kg) are observed at Hg/DOM ratios above approximately 10 $\mu\text{g Hg}/\text{mg DOM}$, coherently with Hg binding to oxygen functional groups [8]. The second issue is that π -electrons

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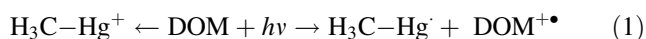
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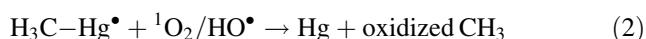
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are loosely bound and they are highly susceptible to radiative excitation [7].

The ligand-to-metal charge transfer could be triggered by the photolysis of the complex $\text{H}_3\text{C}-\text{Hg}^+\leftarrow\text{DOM}$ (where the “ \leftarrow ” indicates electron donation), which could take place as follows (Eq. (1)):



Oxidized DOM ($\text{DOM}^{+\bullet}$) could undergo several processes. Interestingly, similar phenomena involving the charge-transfer photolysis of $\text{Fe(III)}-\text{DOM}$ complexes ultimately cause DOM mineralization via decarboxylation [1]. The species $\text{H}_3\text{C}-\text{Hg}^\bullet$ might, for instance, react with HO^\bullet and/or $^1\text{O}_2$ [1, 2]. Oxidizing transients are expected to preferentially react with the methyl moiety of $\text{H}_3\text{C}-\text{Hg}^\bullet$, because the π -electron bonding system would provide an increased electron density on the methyl group and would lower the excitation energy of the carbon–mercury bond [9]. Such processes would lead to the demethylation of $\text{H}_3\text{C}-\text{Hg}^\bullet$, with the formation of elemental Hg and oxidation of the methyl group (Eq. (2)).



Note that the formation of Hg^{2+} from the reaction (Eq. (2)) would not occur, because irradiated Hg cannot release its outer electron from the s-orbital and also because of the high availability of hydrated electrons in waters under the light condition [7, 10].

The occurrence of inorganic compounds can also be important: for instance, increasing salinity can decrease the photodegradation of CH_3Hg^+ by several processes [3], including: (1) the scavenging of HO^\bullet by bromide (the main HO^\bullet scavenger in seawater) [7, 10] and (2) the different speciation of the CH_3Hg^+ cation in seawater compared to freshwater. In seawater, the formation of stable complexes/ion pairs with anions such as Cl^- and Br^- may hinder the formation of the photolabile species $\text{H}_3\text{C}-\text{Hg}^+\leftarrow\text{DOM}$.

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